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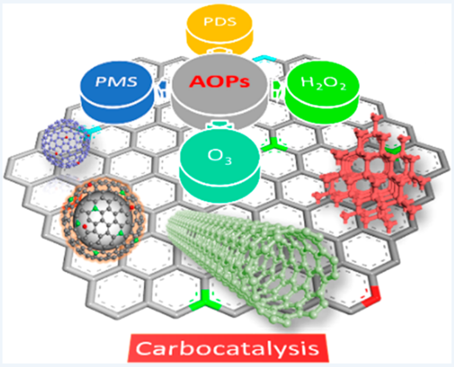
Metal-Free Carbocatalysis in Advanced Oxidation Reactions

Xiaoguang Duan,[†] Hongqi Sun,*[,‡] and Shaobin Wang*[,†]

[†]Department of Chemical Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

[‡]School of Engineering, Edith Cowan University, 270 Joondalup Drive, Joondalup, Perth, WA 6027, Australia



CONSPECTUS: Catalytic processes have remarkably boosted the rapid industrializations in chemical production, energy conversion, and environmental remediation. As one of the emerging applications of carbocatalysis, metal-free nanocarbons have demonstrated promise as catalysts for green remediation technologies to overcome the poor stability and undesirable metal leaching in metal-based advanced oxidation processes (AOPs). Since our reports of heterogeneous activation of persulfates with low-dimensional nanocarbons, the novel oxidative system has raised tremendous interest for degradation of organic contaminants in wastewater without secondary contamination. In this Account, we showcase our recent contributions to metal-free catalysis in advanced oxidation, including design of nanocarbon catalysts, exploration of intrinsic active sites, and identification of reactive species and reaction pathways, and we offer perspectives on carbocatalysis for future environmental applications.

The journey starts with the discovery of peroxymonosulfate (PMS) and peroxydisulfate (PDS) activation by graphene-based materials. With the systematic investigations on most carbon allotropes, for the first time the carbocatalysis for PMS or PDS activation was correlated with the pristine carbon configuration, oxygen functionality (ketonic groups), defect degree (exposed edge sites and vacancies), and dimensional structure. Moreover, an intrinsic difference in catalytic oxidation does exist between PMS and PDS activation. For example, the PMS/carbon reaction is dominated by free radicals, while PDS/carbon catalysis was unveiled as a singlet oxygen- or nonradical-based process in which the surface-activated PDS complex directly degrades the organic pollutants without relying on the generation of free radicals. Nitrogen doping significantly enhances the carbocatalysis because of the positively charged carbon domains, which strongly bind with persulfates to form reactive intermediates toward organic reactions. More importantly, N doping substantially alters the catalytic oxidation from a radical process to a nonradical pathway in PMS activation. Codoping of sulfur or boron with nitrogen at a rational level will synergistically promote the catalysis as a result of the formation of more catalytic centers by improved charge/spin redistribution of the carbon framework. Furthermore, a structure−performance relationship was established for annealed nanodiamonds with a characteristic sp^3/sp^2 (core/shell) hybridization, where the catalytic pathways were intimately dependent on the thickness of the graphitic shells. Interestingly, the introduction of structural defects and N dopants into the well-defined graphitic carbon framework and alteration of graphene/diamond hybrids can transform the persulfate/carbon system from a radical oxidation pathway to a nonradical pathway. Encapsulation of metal nanoparticles within carbon layers further modulates the electronic states of the interacting carbon via charge transport to increase the electron density. Overall, this Account contributes to unveiling the mist of carbocatalysis in AOPs and to summarizing the achievements of metal-free remediation. We also present future research directions on underpinning the knowledge base to facilitate the applications of nanocarbons in sustainable catalysis and environmental chemistry.

■ INTRODUCTION

Confronted with the imperative crisis of energy and natural resources as well as environmental deterioration resulting from industrialization and civilization, the human race never stops seeking state-of-the-art technologies for a sustainable future. In environmental remediation, advanced oxidation processes (AOPs) have been demonstrated as powerful techniques to produce highly reactive oxygen species (ROS) from diverse superoxides for degradation of toxic organic pollutants into harmless mineralized salts, carbon dioxide, and water. Transition metals and oxides of Fe, Co, or Mn have been employed as the most effective activators for peroxymonosulfate (PMS), peroxydisulfate (PDS), hydrogen peroxide (H_2O_2), and ozone to generate sulfate radical ($SO_4^{\bullet-}$), hydroxyl radical ($^{\bullet}OH$), and/or superoxide radical ($O_2^{\bullet-}$).[1] These free radicals possess much higher redox potentials than their parent compounds and can achieve rapid decomposition of a wide range of contaminants.

Recently, carbonaceous materials have stimulated an immense impetus as heterogeneous catalysts because of their metal-free nature and abundance on the earth as well as other merits, such as superior biocompatibility, great resistance toward acid and base, large surface area, and tunable electronic and physicochemical features.[2] Metal-free systems become appealing to overcome the inherent drawbacks of secondary

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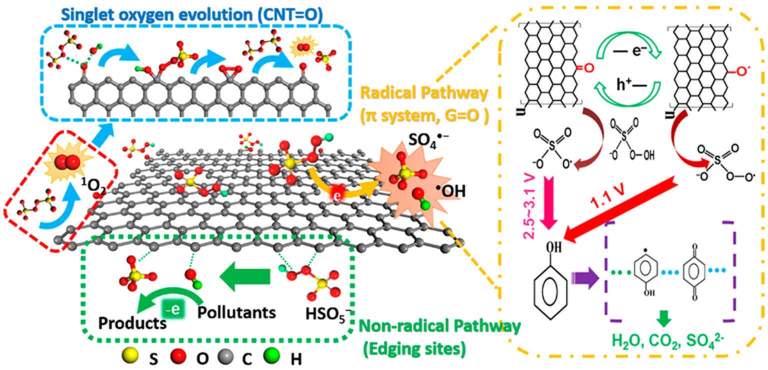

Figure 1. Illustration of activation of PMS on carbocatalysts. Reprinted with permission from ref 11. Copyright 2016 Elsevier.

contamination in metal-based AOPs, such as Fenton and Fenton-like reactions. Since our discoveries of metal-free activation of persulfates (PMS and PDS) by graphene,[3] carbon nanotubes (CNTs),[4] and nanodiamonds,[5] the topic has attracted unprecedented interest and inspired a myriad of studies to harness the state-of-the-art nanocarbons as sustainable catalysts for wastewater remediation. These studies indicated that carbon/superoxide systems involve a variety of reactive species and reaction pathways because of the intrinsic chemical and structural complexity of carbon.[6,7] Hence, this Account focuses on our recent progress in rational materials design, identifying the catalytically active sites, and probing the reactive species and reaction pathways (radical and/or nonradical) by means of both experimental and theoretical investigations. At the end, the research gaps of metal-free AOPs are indicated, and opportunities are proposed for further mechanistic investigations with advanced strategies and applications of carbocatalysis in catalytic oxidation.

METAL-FREE CATALYSTS OF PRISTINE NANOCARBONS

Previously, granular carbonaceous materials like activated carbon, carbon fiber, and biochar have been applied in AOPs, but they demonstrated mediocre performance with poor stabilities. Because of the inherent structural complexity and nonstoichiometric nature of the bulk carbonaceous materials derived from biomass and fossil fuels, the active centers are ambiguous and simultaneously governed by the graphitic degree, oxygen functionalities, porosity, and metal or mineral impurities. This requires insightful understanding of carbon-driven AOPs with simplified configurations, e.g., low-dimensional carbons, to probe carbocatalysis and afford advanced strategies for material optimization.

Reduced graphene oxide (rGO) was first revealed to stimulate PMS to evolve $SO_4^{\bullet -}$ for degradation of phenolics and dyes.[3] The zigzag edges and ketone (C═O) groups at the graphene boundaries were proposed to be chemically reactive. Two carbon systems, carbon spheres and rGOs, were tailored with oxygen functionalities (−C═O, −OH, and −COOH) for catalytic evaluation, and the activity was found to originate from carbonyl groups.[8,9] Density functional theory (DFT) calculations illustrated that PMS ($HO{-}OSO_3^-$) can be only cleaved into $SO_4^{\bullet -}$ over the carbonyl groups on a carbon cluster, confirming the crucial role of quinoidic redox centers.[8,9] As shown in Figure 1, the quinone groups located at the boundaries possess lone-pair electrons and interact with PMS via $C{=}O{-}H{-}O{-}OSO_3$ bonding to weaken the peroxide O−O bond. Hydrogen bonding then delivers electrons from the ketonic oxygen to PMS via inner-sphere charge transfer to produce $SO_4^{\bullet -}$. The metastable and positively charged oxygen center further regains charges from another PMS molecule to produce a monopersulfate radical ($SO_5^{\bullet -}$) and restores the ketone site to fulfill the redox cycle. With respect to the structural defects, a positive correlation was discovered between the reaction rate and the defect degree of graphene samples with distinct loadings of defects and controlled levels of oxygen.[9] Theoretical modeling indicated that the edge sites and vacancies are far more reactive than the honeycomb basal plane to interact with persulfates.[9] Carbon species along the graphene periphery that maintain sp^2 hybridization and confined partial π electrons and spins in a "localized state" are expected to have high catalytic potential.[10]

More interestingly, multiple oxidative pathways upon PMS activation by carbocatalysis were discovered lately. The defective graphene induced a nonradical pathway where radical scavengers barely impacted the oxidative effectiveness.[11] However, similar to metal/PMS systems, the carbon nanotubes and mesoporous carbon only proceed via radical-based oxidation stemming from the semiquinone groups. Theoretical calculations illustrated a moderate electron-transfer tendency and strong adsorption of PMS molecules onto the edge sites to form a reactive intermediate without instantly releasing the sulfate radicals. The activated PMS complex then attacks the electron-rich organic compound by rapid electron abstraction in a nonradical manner. However, the scenarios for CNT/PDS systems turn out to be complicated, and both sulfate radicals[4] and singlet oxygen ($^1O_2$)[12] were identified as reactive species catalyzed by the quinone groups (CNT-C═O). Quinone-like compounds were reported to be able to catalyze persulfate to produce singlet oxygen in an alkaline environment,[13,14] whereas some researchers claimed that ketonic moieties that are intrinsically present on or externally introduced to carbonaceous materials could mediate the formation of singlet oxygen from persulfate irrespective of pH.[12,15] The activated PDS−CNT complex was also proposed to directly attack the target organics in a nonradical process where the conductive carbon matrix served as a charge shuttle between the adsorbed organic (electron donor) and PDS (electron acceptor).[16,17] Moreover, both electron paramagnetic resonance (EPR) tests and DFT calculations evidenced that partial water oxidation occurred on the carbon lattice to promote PDS activation with a prolonged peroxide O−O bond and more electron transfer to produce surface-bound sulfate radicals (another metastable state of activated PDS).[18,19] The physicochemical properties of CNTs and other allotropes are inherently determined by the sources or synthesis procedures with versatile oxygen species and

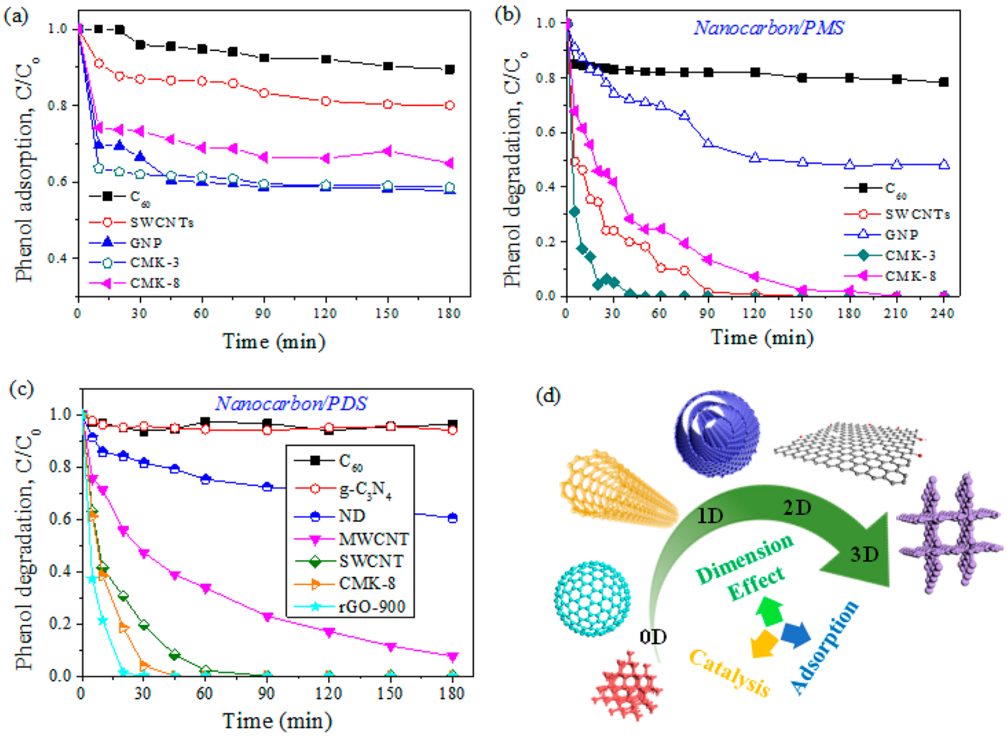

Figure 2. (a) Adsorption, (b, c) catalysis, and (d) illustration of nanocarbons in different dimensions of carbon arrangement. Reprinted with permission from ref 20. Copyright 2015 Elsevier.

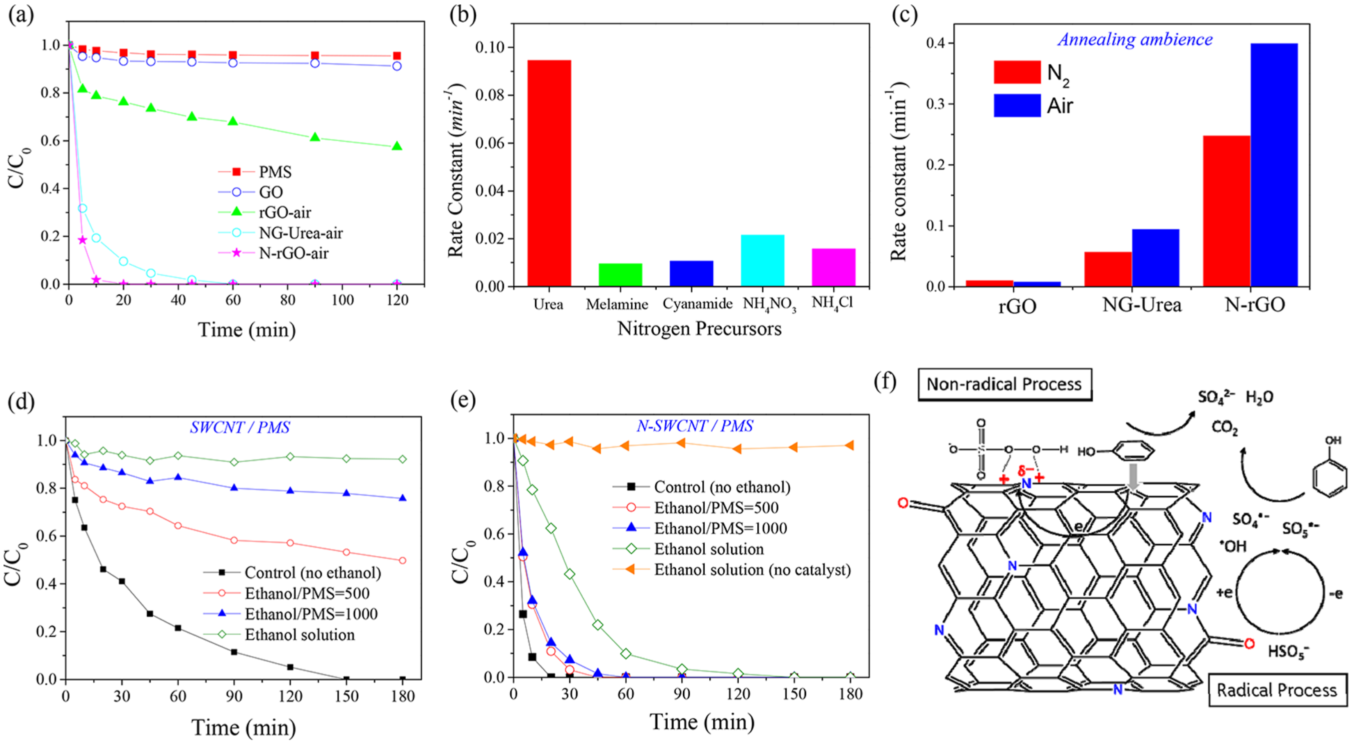

Figure 3. (a) Phenol oxidation on different carbocatalysts with PMS. (b, c) Impacts of (b) nitrogen precursors and (c) annealing ambience of N-graphene. (d, e) Radical quenching impact on (d) SWCNTs and (e) N-SWCNTs. (f) Mechanistic scheme of radical and nonradical processes upon N doping in CNTs. Reprinted with permission from ref 31. Copyright 2017 Elsevier.

surface/edge defects, providing opportunities for multiple reaction pathways. The graphitic degree, chirality, and wall number also govern the electronic conductivity and catalytic potential of CNTs, subsequently influencing the metal-free catalysis.

The carbon configuration and dimension are important factors in carbocatalysis. As shown in Figure 2, adsorption of phenolics was found to be intimately correlated with the molecular arrangement of nanocarbons in the order 0D ≪ 1D ≤ 2D < 3D.[18] The adsorptive capacity of carbonaceous materials is simultaneously governed by the porosity and specific surface area (SSA) by physisorption via $\pi-\pi$ interactions and electrostatic attraction and by the oxygen functionalities by chemisorption via chemical bonding.[20] However, the catalytic performances toward persulfate activation are not necessarily related to the dimensional effect but are active-site- and carbon-configuration-dependent.[18,20] The sp^2-hybridized CNTs and graphene are more catalytically reactive than sp^2/sp^3 fullerene and sp^3 diamond nanocrystals for PMS- or PDS-based oxidation. The delocalized system of π electrons is beneficial for constructing electron-enriched edge/vacancy defects and ketonic groups at the grain boundaries to facilitate redox processes. Peroxide activation can also benefit from the increased SSA and optimal porous structure (CMK-3 and CMK-8) for better access to the catalytic sites in a higher-dimensional scaffold. Besides, the conjugated π system of the graphitic carbon networks might be helpful to activate the aromatic rings of organics by electrophilic attack of the ROS in the nonradical processes. On the basis of the catalytic nature of pristine nanocarbons, thermal treatment and chemical activation have been adopted as efficient strategies to simultaneously tailor the crystalline and porous structures of carbocatalysts and optimize the loading and category of oxygen groups for promoted adsorption and catalysis.[20−22]

■ CHEMICAL MODIFICATION FOR PROMOTED METAL-FREE CATALYSIS

Nitrogen Doping in Carbocatalysis

Tailoring the physicochemical properties of graphene-based materials by introducing foreign atoms (B, N, S, and P) into the carbon matrix can be a feasible strategy to create point defects. The incorporated alien atoms possess a distinct atomic radius and orbitals, electron density, and electronegativity so as to break the chemical inertness of graphene by disrupting the electronic and spin culture of the sp^2-hybridized carbons. However, single doping with boron, phosphorus, sulfur, or iodine was found not to be helpful for graphene-based AOPs,[23,24] whereas nitrogen doping into the carbon lattice gave rise to an astonishing enhancement in PMS activation (Figure 3).[25] The N doping was also discovered to simultaneously improve the adsorption capacity and catalytic activity of PDS activation for degradation of aqueous phenols and antibiotics.[26,27] Nitrogen modification introduces different N dopants (graphitic, pyridinic, and pyrrolic N) and N functionalities (oxynitride and aminated groups) for varying carbocatalysis. Slight doping with pyridinic and pyrrolic N (0.8 atom %) manifested better performance than with pristine CNTs, and graphitic N at a similar doping level would further boost PMS activation.[4,28] The better catalytic performance of N-doped graphene (N-graphene) was favored by a higher proportion of quaternary N atoms.[25]

Theoretical investigations of PMS adsorption onto different doping models suggested that graphitic N presented the greatest electron-transfer capacity and lowest adsorption energy among the dopants because the substitutional N doping was able to tailor the charge distribution of adjacent carbons because of the higher electronegativity ($\chi_N = 3.04$ vs $\chi_C = 2.55$).[25] These polarized carbons manifest a better affinity for bonding to the negatively charged oxygen atoms in persulfate to activate or cleave the peroxide O−O bond. Then charge transfer is expected from the electron-rich nitrogen atoms to persulfate molecules via the carbon−N(−)−C(+)—O(−)−peroxide bridge to produce ROS. Pyrrolic and pyridinic nitrogen, which have lone-pair electrons (similar to ketones), can serve as unpaired stable radicals to capture the electrophilic species of peroxide. Additionally, surface functionalization with amine groups ($-NH_2$) as electron-donating functionalities also promotes catalytic activity compared with unmodified graphene for PDS activation but not comparable to the N-doped graphene.[29] However, oxynitride groups ($-NO_x$) in passivated carbocatalysts were ineffective for catalytic reaction.[25,28]

Currently, graphene oxide (GO) has been universally employed as a classic carbon hosting material for molecular engineering. GO is functionalized with a massive amount of oxygen moieties (up to 40 atom %) and can provide an open platform for N doping in the presence of nitrogen precursors. These oxygen groups play a vital role in accommodating N atoms into the carbon lattice via either directly bonding with N precursors or undergoing thermal decomposition to react with the N precursors. Altering the annealing temperature can manipulate both the N-doping level and category for an optimal metal-free catalyst because of the distinct thermal stabilities of N dopants.[25,30] Therefore, the impacts of carbon/nitrogen precursors and the annealing ambience were also investigated to attain N-graphene with satisfactory performance.[31] Urea has been demonstrated as the most promising N precursor compared with inorganic salts (NH_4NO_3 and NH_4Cl) and organic compounds (melamine and cyanamide). Thermal decomposition of urea would generate gaseous CO_2 (structure and chemical modifier) and NH_3 (reductive and doping agent), giving rise to an optimized porous structure, desirable N-doping level, reduction degree, and surface acidity/alkalinity.[31,32]

More importantly, N-graphene/persulfate systems can induce nonradical reactions[31,33−35] It was found that even a minor level of N doping (0.8 atom %) could impressively boost phenol decomposition and completely alter the oxidative pathway from a radical process (CNT/PMS) to a nonradical oxidation (N-CNT/PMS).[28,36] The superoxides (electron acceptors) were suggested to strongly bond with positively charged carbon atoms adjacent to N dopants to form a reactive complex (persulfate−carbon) or surface-confined radicals. The metastable intermediates subsequently oxidize the organic contaminants (electron donors) via electron abstraction through the carbon lattice (electron shutter) or inner-sphere interaction (oxidant−organic bonds). Moreover, the nonradical reactive species are confined at the carbon interface and exhibit a moderate oxidizing potential and particular selectivity toward organics, in contrast to sulfate radicals, which tend to attack organics with unsaturated bonds and aromatic structure especially at their neutral structures, or the nonselective hydroxyl radicals. The nature of the organic substrate can partially influence the oxidative efficiency of the nonradical reaction. A linear correlation of adsorption and degradation was established, where the adsorptive process is the rate-limiting step for catalytic removal of phenolic substances in N-graphene/PDS.[26] In addition, the ionization potential of the organic and the redox state of the oxidized product after the first-step oxidation cooperatively set a threshold for the oxidative capacity of nonradical processes, which is determined by the electron-donating/withdrawing substituent groups on the aromatic ring.[37] Thus, the charge density of the organic is a crucial factor in determining the adsorption onto the carbon network and regulating the charge transport from the organic to the electrophilic persulfate−carbon complex, making

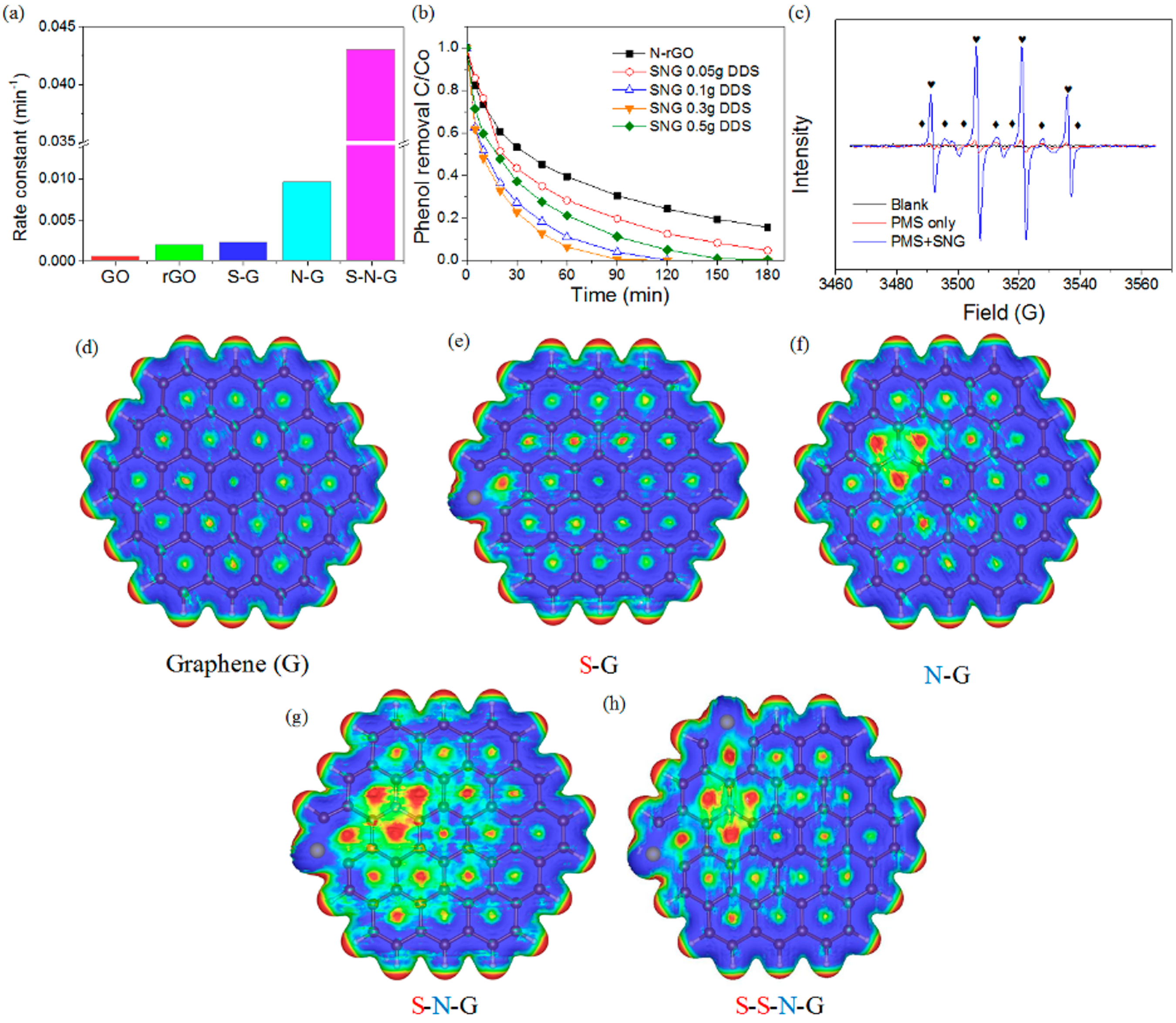

Figure 4. (a) Rate constants for phenol oxidation on different carbocatalysts. (b) Impact of sulfur precursor loading. (c) EPR spectrum of the SNG/PMS system. (d−h) Electrostatic potential distributions of (d) graphene, (e) S-G, (f) N-G, (g) S-N-G, and (h) S-S-N-G. Reprinted with permission from ref 24. Copyright 2015 Wiley.

electron-rich substances (phenolics, antibiotics, and dyes) to be mostly degradable in the nonradical systems.[16,26,37,38]

Boron/Sulfur- and Nitrogen-Codoped Graphene

The introduction of a secondary adventitious atom besides nitrogen can produce new features on graphene. For instance, trace boron (0.1 wt %) discernibly promoted N-graphene catalysis of PMS activation, whereas an inferior activity appeared when the boron content was increased to 0.25 wt %.[39] Both experimental and theoretical studies revealed that a synergistic effect of B and N codoping is governed by the loading and relative position of boron with respect to the host dopant (N) in the carbon network.[40] Formation of a close B−C−N heterostructure in the conjugating π network can greatly activate both carbon and boron with a coupling effect, meanwhile inhibiting the direct neutralization of N (charge donor) and B (charge acceptor) at the ortho position to preserve both active centers. The codopants result in a dipole moment where the boron atoms facilitate the chemical bonding with persulfate and nitrogen dopants contribute to the charge transfer, cooperatively leading to the accelerated metal-free oxidation.

Additionally, S and N codoping also exhibited a synergistic effect for enhanced catalysis compared with sole doping.[24] As illustrated in Figure 4, N doping can effectively break the chemical inertness of graphene by interrupting the spin and charge distributions of the uniform sp^2-hybridized configuration, and codoping with an optimal level of sulfur at the geometric defects can further modulate the domain.[24] The second dopant (S) is able to activate the carbon atoms adjacent to nitrogen with a higher electron and spin density, giving rise to a more intimate interaction with PMS to lower the energy barrier for generation of reactive species.[24,41] Besides, the positively charged regions are impressively enlarged by codoping through the synergistic effect, which is advantageous for providing larger catalytic areas to interact with organics and peroxides for the accelerated adsorption and oxidation. However, overloading of the sulfur dopant suppresses the

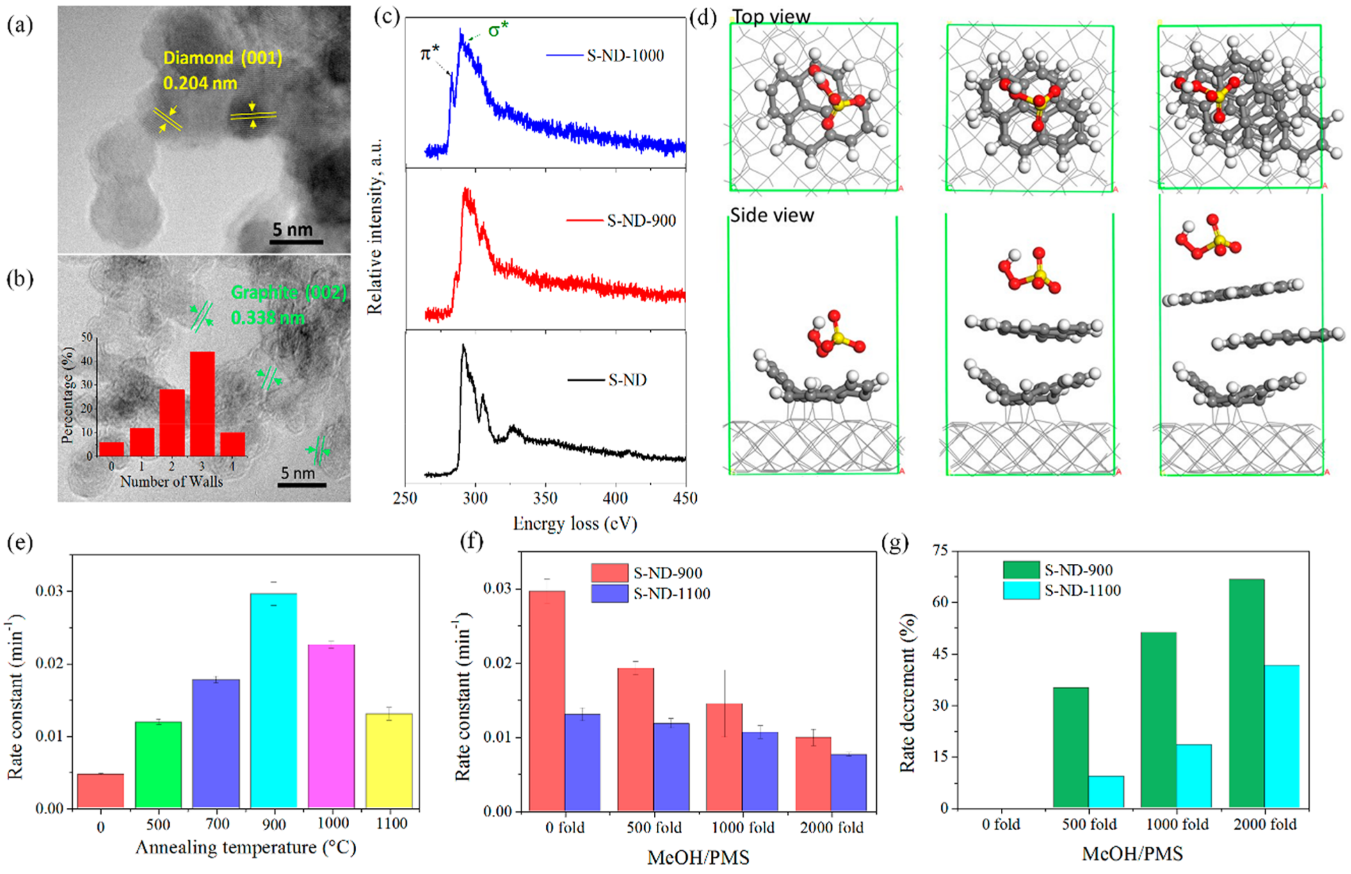

Figure 5. (a, b) TEM images and (c) EELS spectra of graphitized nanodiamond. (d) Theoretical modulation of nanohybrids with different graphitic layers. (e) Impact of annealing temperature on catalysis. (f, g) Quenching effect on catalytic oxidation on nanodiamonds with different graphitic degrees. Reprinted with permission from ref 45. Copyright 2018 Elsevier.

synergistic effect as a result of the redistribution of electrons/spins and an unbalanced π system.[24,42] As a result, both the doping level and distribution of the dopants should be carefully controlled in a single- or dual-doped carbon scaffold for desirable environmental catalysis.

■ NANOCOMPOSITES: TWO COMPONENTS MAKING A GREAT DIFFERENCE

Carbon/Carbon Hybrids

Construction of nanohybrids from primary nanocarbons can both enlarge the number of catalytic sites and tailor the catalytic centers. Thermal annealing of diamond nanocrystals (5−10 nm) results in a characteristic core/shell structure due to the collapse and refabrication of the diamond outer sphere (sp^3-hybridized carbon) into a strained graphitic layer (sp^2-hybridized carbon). The graphitized nanodiamonds (G-NDs) then deliver the physicochemical properties of graphene-based materials while the diamond core imbues the curved graphene with new properties. Herein, the fascinating sp^2/sp^3-hybridized architecture may bring in novel features for metal-free catalysis.

Pristine bulk nanodiamonds (NDs) with pure sp^3 hybridization were unveiled to be less active in PMS/PDS-based oxidation, while G-NDs exhibit superb performance to initiate PMS and PDS activation (Figure 5).[11,19] Thermal treatment removes the amorphous carbon and soot covering the NDs and tunes the reducibility of the graphitic shell of the composites for electron transfer to persulfates to generate reactive species. PDS was proposed to be activated as either a metastable PDS−carbon complex or confined sulfate radicals on G-NDs.[19,43] The graphitic layer then acts as an electron tunnel for rapid charge transport from the adsorbed organic to the surface-bound reactive species via a nonradical pathway to accomplish the oxidation.[44] More recently, deliberate material/experimental design and theoretical predictions revealed synergistic structure−activity chemistry of PMS activation on G-NDs.[45] The radical quenching tests and advanced characterizations showed that augmenting the wall number at higher annealing temperatures would give rise to more graphitic shells and transform a radical-dominated oxidation (S-ND-900) to a nonradical pathway (S-ND-1100).[45] The theoretical calculations revealed that the diamond core would excite electrons to the graphitic shell of one-layer graphene/diamond via strong covalent bonds, leading to a denser electron population of the carbon sphere, which would promotes the charge migration to PMS to produce sulfate radicals.[5,45] However, electrons cannot penetrate multiple shells in a three-layer graphene/diamond model, giving rise to a greater adsorption energy of PMS on the outermost layer of the hybrid to form a surface-activated complex for nonradical oxidation. Further modification of the graphitic shell by N doping can attract more charges from the diamond substrate, giving rise to a highly reactive surface for reinforced carbocatalysis.[5]

Carbon-Wrapped Metal Composites

Transition metals such as iron and nickel can serve as catalysts to fabricate carbon precursors into a well-defined graphitic matrix (graphene or carbon nanotubes) with metal nanoparticles embedded beneath the carbon layer, providing an appealing strategy for scalable production of nanocarbon catalysts.[46] The synthesized N-doped carbon nanotubes (N-CNTs) with encapsulation of zero-valent iron,[47] cobalt,[48] and nickel[49] nanocrystals exhibited superior catalytic performances compared with the sole metals and CNTs for PMS-based oxidation with excellent stability. In the carbon−metal composites, the wrapped metal clusters interact with the inner sphere of graphitic carbon. Such a configuration decreases the local work function of the outer carbon surface and lowers the adsorption hindrance for activation of persulfates via electrostatic or covalent interactions.[50] Effective charge transport from the metal nanoparticles to the attached π system via Me−N−C or Me−O−C bonds gives rise to denser local electronic states of the carbon surface at the interaction region. Then the activated domain would break the peroxide O−O bond in persulfate and transfer the electrons to evolve reactive radicals for catalytic oxidation. Similarly, N doping in the carbon lattice is beneficial for the electron migration from metal crystals. These features synergistically regulate the electronic and chemical properties of the carbon surface to stimulate the peroxide bonds by generating radical/nonradical reactive species for mineralization of contaminants.

Other metal species such as metal carbides (Fe_2C, Ni_3C) and manganese nitride (MnN_4) can also improve the catalytic activity of the coating graphitic carbon lattice.[51−54] The intrinsic impacts of wrapped metals on carbocatalysis may lie in the size, category, and/or surface coordination chemistry of the metal species. The bonding bridge and electron-transfer capacity between metal and carbon synergistically determine the charge density of the outer graphene layers toward manipulated carbocatalysis. Additionally, the encapsulated metal particles (Co, Mn, Fe, and Ni) endow the nanocarbons with *magnetic properties*, which are favorable for magnetic separation and recycling of the carbocatalysts. Meanwhile, the carbon layers protect the metal particles from corrosion and leaching into the surrounding water. Nevertheless, trace-level metal residues can be incorporated into the carbon planar surface that are hardly detectable by elemental analysis or eliminated by acid pickling, and thus, their impacts cannot be simply ruled out in metal-free catalysis.[55]

■ NATURE OF CARBOCATALYSIS IN ADVANCED OXIDATION

The decisive factor for catalytic activation of persulfates lies in activation of the peroxide O−O bond and charge transport between the peroxide and catalyst to evolve reactive species. In metal-based catalysis, transition metals/oxides with variable valence states can easily coordinate the redox processes, determined by the geometric/electronic effect of the exposed facets. The metal ions interact with water to form surface hydroxyl groups for bonding with persulfates via hydrogen bonding to deliver electrons and generate free radicals. Distinctively, the hydrophobicity of carbon enables the direct interaction of PMS/PDS to weaken the peroxide O−O bond by the conjugated π system. As an intact and catalytic matrix, the conductive carbon lattice serves as a tunnel to facilitate charge transport from adsorbed organics to the activated peroxide/carbon complex due to the redox potential differences. Herein, the nonradical oxidation is a domain-based catalysis that is more selective toward organics with high charge density for electrophilic attack, and sp^2-hybridized nanocarbon is more reactive than sp^3-hybridized and amorphous carbons for adsorption and electron transfer.

However, practical nanocarbons are inherently produced with point defects such as edges, vacancies, oxygen functionalities, and incorporated alien atoms. These defect sites can disturb the homogeneous and inert carbon network with high chemical potentials, thus dominating the catalytic oxidation with new features. For instance, the edge defects and positively charged carbons resulting from N doping exhibit strong binding affinity with persulfates to form reactive complexes to promote the nonradical oxidation, whereas the electron-rich ketones can serve as Lewis basic sites to directly transfer electrons to persulfates to produce free radicals or singlet oxygen. Herein, excessive oxygen functionalities are not desirable because they will not only occupy the edges and prevent the reaction with peroxides via steric hindrance but also decrease the reductive degree of the carbon lattice, which determines the charge-transport capacity within the graphitic carbon lattice and influences the electron population of edge carbons and ketones toward the redox reaction.[11,18] The encapsulation of metal or diamond crystals beneath carbon shells can modulate the charge/spin culture of the interacting region, which impacts the bonding strength and electron transfer between the activated carbons and persulfates. This is also affected by the thickness of the coating layers, which regulates the charge-delivery efficiency at the interfaces and the reactivity of the outermost carbon surface of the hybrids toward the radical reaction at electron-dense regions or nonradical oxidation with strong adsorption sites for generation of PMS/PDS−carbon activated intermediates. Therefore, the structure/chemistry−performance relationship and optimization of the dominant catalytic sites and reaction pathways are of great significance to a highly efficient carbon-based AOP system. Fabrication of efficient carbocatalysts requires rational manipulation of both the carbon structure and surface chemistry.

■ CONCLUSIONS AND PROSPECTS

Nanocarbons have demonstrated promise as metal-free catalysts for catalytic superoxide activation and oxidation. The green system, compared with metals, overcomes the inherent drawbacks of secondary contamination without compromising the efficacy. Deliberate material design and theoretical calculations have been integrated to achieve a comprehensive understanding of the carbocatalysis and reaction pathways in AOPs. Surface modifications of pristine nanocarbons with heteroatom doping and construction of nanohybrids impressively boost the catalytic performance by creating/tailoring the active sites and electronic structures of the carbocatalysts. However, the high cost of the nanocarbons for commercial applications poses imperative demands to exploit novel strategies for scalable production of high-quality graphitic carbon materials with robust structures as cost-effective and green environmental catalysts.[56,57]

Precise manipulation of the carbon configuration, defect degree, and surface chemistry within a porous framework is critical for efficient carbocatalysis for superoxide activation. State-of-the-art atom-scale and in situ surface characterizations are also advantageous tools for insightful mechanisms in future studies. Theoretical calculations are fascinating strategies to simplify the carbon matrix to exclusively identify the roles of carbon configuration, defects, heteroatom doping, and oxygen functionalities at different levels and the species in persulfate activation as well as the synergistic effects among them. An in-

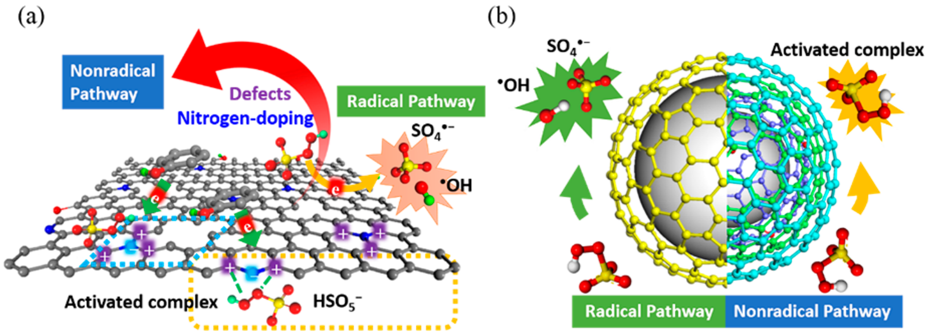

Figure 6. Illustrations of radical and nonradical oxidations on (a) graphene and (b) graphitized nanodiamond. Reprinted with permission from refs 31 and 45. Copyright 2017 and 2018 Elsevier.

depth understanding of the origins of radical and nonradical pathways as well as the evolution of different reactive species should be developed from a molecular level.

Interestingly, the nonradical pathway in carbocatalysis with a moderate oxidative capacity, different from most metal catalysts, can be harnessed for rapid mineralization of organic contaminants in real wastewater matrixes and natural systems with the presence of diverse radical scavengers, such as natural organic matter, inorganic ions, alcohols, or high salinity. Additionally, the redox potential of the carbon/persulfate system is maneuverable from a nonradical pathway (mild and selective oxidation) to radical processes (deep and nonselective oxidation) simply by altering the doping/defect level or the composite components, as shown in Figure 6, offering a promising platform for disinfection, hydrocarbon conversion, and selective oxidation in organic chemistry.

■ AUTHOR INFORMATION

Corresponding Authors

*S.W.: E-mail: shaobin.wang@curtin.edu.au. Phone: +61 8 9266 3776.
*H.S.: E-mail: h.sun@ecu.edu.au. Phone: +61 8 6304 5067.

ORCID

Xiaoguang Duan: 0000-0001-9635-5807
Hongqi Sun: 0000-0003-0907-5626
Shaobin Wang: 0000-0002-1751-9162

Notes

The authors declare no competing financial interest.

Biographies

Xiaoguang Duan received his Ph.D. in Chemical Engineering from Curtin University in Australia in 2016. He currently works as a postdoctoral fellow at the same university. He has been dedicated to seeking feasible applications of nanocarbon materials in environmental science and facilitating mechanistic insights and innovation of carbocatalysis with advanced protocols.

Hongqi Sun received his Ph.D. in Chemical Engineering at Nanjing University of Technology in China. He is now a Full Professor of Chemical Engineering and Vice-Chancellor's Professorial Research Fellow at the School of Engineering of Edith Cowan University in Australia. His research focuses on the synthesis of nanostructured materials for solar energy utilization and environmental nanotechnology. He also serves as an Associate Editor of *RSC Advances* and the *Journal of Advanced Oxidation Technologies*.

Shaobin Wang obtained Ph.D. from the University of Queensland in Australia. He is a John Curtin Distinguished Professor in the Department of Chemical Engineering at Curtin University. His research interests focus on the synthesis and applications of nanomaterials for carbon dioxide utilization, energy conversion, and environmental remediation. He has published over 300 refereed journal papers with over 20 000 citations and an H-index of 77 and served as an editorial board member for several international journals.

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